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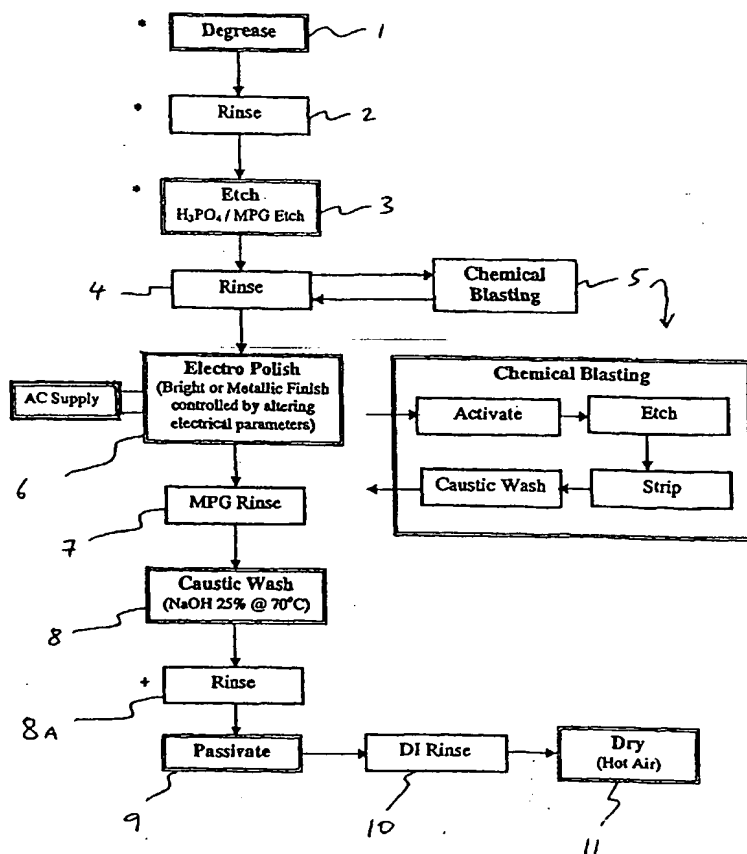
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(54) Title: SURFACE TREATMENT OF MAGNESIUM AND ITS ALLOYS



(57) Abstract: Methods of polishing and/or brightening surfaces of magnesium or magnesium alloy are disclosed. Polishing and/or brightening methods suitable to both high and low aluminium content magnesium articles (13) are disclosed. In each of the methods, the surface is polished (step 6) and then passivated (step 9). Using the disclosed methods it is possible to control aspects of the appearance of the surface to thereby, for example, obtain a bright and shiny surface to a magnesium or magnesium alloy article (13) which is both stable and corrosion resistant. It is also possible to provide a predetermined texture to the surface using optional steps (step 5).



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## THE SURFACE TREATMENT OF MAGNESIUM AND ITS ALLOYS

**TECHNICAL FIELD**

The present invention relates to surface treatment of magnesium and its alloys and in particular, though not solely, this invention relates to providing a bright shiny and/or textured surface finish to magnesium or magnesium alloy.

**BACKGROUND ART**

Magnesium metal, either pure or in an alloy form, is a highly reactive metal. In its usual fabricated forms the surface appearance is relatively dull and obscured by surface oxidation products or other compounds. Accordingly, magnesium metal does not usually manifest a bright, shiny, metallic finish except when the article has been machined. Although a dull surface may not always be disadvantageous, it is often desirable to provide a bright or polished surface to magnesium for reasons of aesthetics or utility. Owing to the reactivity of magnesium, post-treatments are generally necessary to passivate the surface, and conventionally the desired surface finish is lost during this step.

Conventional treatment of magnesium and its alloys has mostly consisted of treatments that result in an anodic coating being applied to the metal, or a paint film, following some kind of pre-treatment process intended to promote paint adhesion. Mostly these processes neither brighten nor polish the metal. Anodising processes for magnesium differ from those employed for aluminium in that the resulting surface is opaque and frequently the coating is inherently coloured. While in many applications this may be a desirable finish in itself, this is not regarded as surface polishing or brightening.

Techniques for applying paint to magnesium or its alloys comprise in the main pre-treatments such as chromating or non-chromating conversion treatments, followed by application of a paint. The paint may be in the form of a powder coat, which is electrostatically applied then oven-cured, or a wet paint. The painted surface may have a shiny finish, but it is not a finish that is comparable to a shiny metallic surface.

Techniques for chemically or electrochemically brightening other metals exist. Methods for brightening aluminium alloy articles are commonly employed in anodising plants. However, these techniques are not applicable to magnesium alloys due to their different chemistry.

For example, an approach to brightening aluminium involves a combined acid mixture in which magnesium articles would dissolve rapidly.

Many different metals and alloys of aluminium can be brightened by either chemical or electro-chemical methods. Although, many brightening methods have been known for a long time, little work has been made to accommodate magnesium and its alloys.

Two other problems exist that make the processing of magnesium and magnesium alloys difficult. Firstly, many commercial alloy articles (especially die cast articles) exhibit significant amounts of segregation both of the surface and in the interior of the article. This together with commonly encountered casting defects produces a highly inhomogeneous surface which cannot be improved by conventional means. Secondly, as magnesium is a highly reactive metal that forms a non-continuous oxide layer, for a viable bright surface finish to be attained the surface must be treated in a manner to prevent the oxide layer forming after surface brightening or polishing treatments. Traditionally such treatments include films or coatings which are opaque and/or are produced using heavy metals and other undesirable toxic chemicals.

It is also possible in some circumstances to chemically or electrochemically plate other metals, for instance, nickel, onto magnesium substrates. Although the resulting plated article has a shiny, metallic appearance, this is due to the plated metal and could not be regarded as a system for brightening or polishing magnesium or magnesium alloy articles. There are also profound disadvantages in plating other metals onto magnesium or magnesium alloy substrates including for example galvanic corrosion problems in corrosive environments, expense, processing difficulties in a plating process and high reject rates from most processes.

It is therefore an object of the present invention to provide a surface treatment for magnesium and its alloys which will go at least some way towards addressing the foregoing problems or at least to provide the industry and/or public with a useful choice.

All references, including any patents or patent applications cited in this specification are hereby incorporated by reference. No admission is made that any reference constitutes prior art. The discussion of the references states what their authors assert, and the applicants reserve the right to challenge the accuracy and pertinence of the cited documents. It will be clearly understood that, although a number of prior art publications are referred to herein, this reference does not constitute an admission that any of these documents form part of the common general knowledge in the art, in New Zealand or in any other country.

It is acknowledged that the term 'comprise' may, under varying jurisdictions, be attributed with either an exclusive or an inclusive meaning. For the purpose of this specification, and unless otherwise noted, the term 'comprise' shall have an inclusive meaning - i.e. that it will be taken to mean an inclusion of not only the listed components it directly references, but also other non-specified components or elements. This rationale will also be used when the term 'comprised' or 'comprising' is used in relation to one or more steps in a method or process.

Further aspects and advantages of the present invention will become apparent from the ensuing description which is given by way of example only.

## 10 DISCLOSURE OF INVENTION

Accordingly, in a first aspect the invention consists in a method of polishing and/or brightening a magnesium or magnesium alloy surface comprising the steps of:

- i) polishing the surface, and
- ii) passivating the polished surface.

- 15 Preferably, the method comprises an initial step of pre-treating of said surface to remove surface contaminants.

Preferably, said pre-treatment step comprises chemically etching said surface and/or degreasing said surface.

- 20 Preferably, surface contaminants are removed prior during the pre-treatment step by contacting said surface with one or more degreasing components, such as sodium hydroxide.

Preferably, said chemical etching component comprises a nitric acid and/or phosphoric acid.

Preferably, said pre-treatment step includes chemically blasting said surface.

- 25 Preferably, said polishing step is carried out by a chemical polish and/or electro-chemical polish while said surface is immersed in a polishing composition.

Preferably, said chemical polish and/or electro-chemical polish removes surface layers and/or reduces microscopic high points from the surface.

Preferably, said polishing step is carried out by immersing said surface in a bath comprising one or more of the following components; a phosphoric acid solution, monopropylene glycol, ethylene glycol, and nitric acid.

Preferably, said electro-chemical polish is a galvanic electrolysis.

- 5 Preferably, said electro-chemical polish further includes the supply of an external voltage to said surface.

Preferably, during said electro-chemical polish step an electrolyte anti-stagnation means is utilised or an AC voltage is applied to the electrolyte containing said surface.

- 10 Preferably, said electrolyte anti-stagnation means is an electrolyte stirrer and/or an ultrasonic wave generating means.

Preferably, said polishing step is followed by an intermediary wash removing at least some of the chemical and/or electrolyte solution from said surface.

Preferably, said intermediary wash is carried out in a composition containing monopropylene glycol and/or ethylene glycol.

- 15 Preferably, said polishing step and/or said intermediary wash is followed by an alkaline wash.

Preferably, said alkaline wash is carried out in a composition containing sodium hydroxide.

Preferably, said alkaline wash substantially neutralises acids and/or substantially removes Aluminium, Manganese or Zinc from said surface.

- 20 Preferably, said passivating step provides a substantially corrosion resistant and/or water insoluble surface coating or film.

Preferably, said substantially corrosion resistant and/or water insoluble surface coating or film is a phosphate salt coating or film.

- 25 Preferably, an inorganic material coating or sealer is applied to said substantially corrosion resistant and/or water insoluble surface coating or film.

Preferably, said inorganic material coating or sealer is substantially transparent and/or substantially provides corrosion protection and/or at least some protection from mechanically induced damage.

Preferably, said inorganic material coating or sealer is a silicon based composition, such as a disodium metasilicate, and a polyacrylamide coagulant in de-ionised water.

Preferably, said passivating step and/or said inorganic material coating or sealer step is followed by a surface drying step.

5 Preferably, wherein a chemical blasting step comprises the steps of:

- a. immersing the surface in an iron based solution,
- b. activating said surface with said iron based solution, wherein said iron based solution is reduced to thereby deposit iron on said surface,
- c. etching said surface with an etch composition to modify the activated surface layer,
- 10 d. stripping iron deposits from said surface with an iron removal composition, and
- e. washing said surface to substantially remove compositions remaining on said surface.

15 Preferably, said activator is a solution selected from the following; ferric chloride, hydrochloric acid, ammonium bifluoride, and ammonium bromide.

Preferably, said etch composition is selected from the following; ferric chloride; ferric chloride and phosphoric acid solution, or a reduced solution of ferric chloride and phosphoric acid.

20 Preferably, said iron removal composition is selected from the following; nitric acid and sodium borate in solution, or nitric acid and phosphoric acid in solution.

Preferably, said step of washing said surface is carried out with a water wash or an alkaline wash.

#### BRIEF DESCRIPTION OF DRAWINGS

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Further aspects of the present invention will become apparent from the following description which is given by way of example only and with reference to the accompanying drawings in which:

30 Figure 1 illustrates a process flow diagram of various process steps of one embodiment according to the present invention, and

Figure 2 illustrates a passivation cell configuration of an embodiment according to the present invention.

### **BEST MODES FOR CARRYING OUT THE INVENTION**

A set of method steps for chemically and/or electro-chemically brightening or texturing (also termed "polishing" herein) the surface of articles composed of magnesium or its alloys are described herein. The steps making up the processes by which the articles are polished as well as compositions of the chemical solutions that are used from the present invention. The following description is accordingly given by way of example only and it should be appreciated that a number of functional equivalents can be substituted for the compositions.

10 With reference to the drawings and in particular Figure 1, a flowchart of various steps involved in the polishing and/or brightening of a magnesium or magnesium alloy surface is shown.

Prior to processing, it is usually appropriate to pre-treat (steps 1 to 4) magnesium or magnesium alloy articles to clean and prepare the surfaces for brightening or polishing. The treatment depends on alloy, and the most preferred treatments are summarised below for some common alloys and forming processing. Alternative treatments may be possible and in some cases, depending on the original surface condition of the article, the omission of one or more steps may be possible without adverse effect on subsequent processing steps.

This invention discloses a means for processing and treating magnesium or magnesium alloys to preferably generate cosmetically acceptable bright textured surfaces which may be overlaid with an inorganic, transparent and/or corrosion resistant film. With reference to Table 1 examples of possible compositions (or process solutions and preferred operating conditions) for the surface treatment processing steps, subsequently to be described are set out. Table 2 illustrates possible pre-treatment process steps (and operating conditions) for a number of commonly utilised alloys. Table 3 provides a useful summary of some combinations of process steps (from Table 1) and their sequencing for treating the surface of magnesium or magnesium alloys.



TABLE 1: PROCESS SOLUTIONS

Name	Code	Composition	Temperature
Phosphoric etch	PE3	Phosphoric acid ( $H_3PO_4$ ) – 10 mol/l Nitric acid ( $HNO_3$ ) – 0.5 mol/l	Ambient
Electropolishing solution	EP3	Phosphoric acid ( $H_3PO_4$ ) – 10 mol/l Monopropylene glycol ( $C_3H_8(OH)_2$ ) – 4.5 mol/l	25-35 °C
Washing solution	PG1	Monopropylene glycol – 100%	40-60 °C
Caustic washing solution	CW25	Sodium hydroxide (NaOH) – 6.25 mol/l	70 °C
Passivator 1	PM1	Potassium permanganate ( $KMnO_4$ ) – 0.25 mol/l Phosphoric acid ( $H_3PO_4$ ) – to adjust pH to 5-5.5 (added as 5% $H_3PO_4$ )	15-30 °C
Passivator 2	PC1	Chromic acid ( $CrO_3$ ) – 1.8 mol/l Ferric nitrate ( $Fe(NO_3)_3 \cdot 9H_2O$ ) – 0.1 mol/l Potassium fluoride (KF) 0.07-0.15 mol/l	15-30 °C
Chemical blast solution	CB1	Ferric chloride ( $FeCl_3$ ) – 0.12 mol/l Phosphoric acid ( $H_3PO_4$ ) – 0.8 mol/l	Ambient
Improved chemical blast Solution	CB2A	Ferric chloride ( $FeCl_3$ ) – 0.16 mol/l Hydrochloric acid (HCl) – 0.05 mol/l Ammonium bifluoride ( $NH_4HF_2$ ) – 0.06 mol/l Ammonium bromide ( $NH_4Br$ ) – 0.17 mol/l	Ambient

**TABLE 2: RECOMMENDED PRE-TREATMENTS**

Forming Process	Alloy	Pre-treatment Steps		
		Description	Compound	Conditions
Die casting (for bright or metallic finish)	AZ91	Degrease Rinse Phosphoric Etch Rinse	CW25 H <sub>2</sub> O PE3 H <sub>2</sub> O	1-2 min  30-60 seconds
Die casting (for bright or metallic finish)	AM50/60	Degrease Rinse Phosphoric Etch Rinse	CW25 H <sub>2</sub> O PE3 H <sub>2</sub> O	1-2 minutes  30 seconds
Rolled sheet (for bright or metallic finish)	AZ31	Degrease Rinse Phosphoric Etch Rinse	CW25 H <sub>2</sub> O PE3 H <sub>2</sub> O	1-2 minutes  Up to 2 minutes
Extrusion (for bright metallic finish)	AZ31	Degrease Rinse	CW25 H <sub>2</sub> O	1-2 minutes
All alloys (chemically blasted finish)		As for bright metallic finish plus: Rinse Rinse	CW25 H <sub>2</sub> O	30-45 seconds

**TABLE 3: SUMMARY OF PROCESS SEQUENCE FOR ELECTROPOLISHING, METALLIC FINISH AND CHEMICAL BLAST FINISH**

Forming Process	Alloy	Finish	Process steps		
			Description	Compound	Conditions
1. Chemical blasting					
(a) Die casting Extrusion Rolled sheet	AZ91	Chemical blast	Activation	CB2A	1 minute
	AM50		Chemical blasting	CB1	2-10 minutes
	AM60		Chemical blasting 2	CB2A	1 minute
	AZ31		Caustic wash	CW25	1-2 minutes
			Rinse	H <sub>2</sub> O	
(b) Extrusion Rolled sheet	AZ31	Chemical blast	Same as (a) above, then Phosphoric etch	PE3	1.5-2.5 minutes
			Rinse	H <sub>2</sub> O	
2. Electropolish					
Die casting	AZ91	Bright finish	No Chemical blasting	EP3	8 minutes
			Galvanic polish	EP3	15-20 seconds
			AC current		

		Chemical blast	Same as (a) above, then: AC current Galvanic polish AC current	EP3	2 minutes
				EP3	3-4 minutes
				EP3	15-20 seconds
	AM50 AM60	Bright finish	No Chemical blasting Galvanic polish AC current	EP3	6 minutes
				EP3	15-20 seconds
Rolled sheet		Chemical blast	Same as (a) above, then: AC current Galvanic polish AC current	EP3	1 minute
				EP3	2-3 minutes
				EP3	15-20 seconds
	AZ31	Bright finish	No Chemical blasting Galvanic polish AC current Galvanic polish AC current	EP3	30 seconds
				EP3	10 seconds
				EP3	20 seconds
				EP3	10 seconds

Extrusion	AZ31	Bright finish	No Chemical blasting Galvanic polish AC current	EP3 EP3	50-60 seconds 10 seconds
		Chemical blast	Same as (a) or (b) above steps then as for bright finish	EP3 EP3	50-60 seconds 10 seconds
		Metallic finish	Galvanic polish	EP3	4-5 minutes Note: No AC current
Die casting	AZ91	C-blast metallic	Same as (a) above then: Galvanic polish	EP3	3-5 minutes
		Metallic	Galvanic polish	EP3	3.5-4 minutes
	AM50	CB metal	Same as (a) above then galvanic polish	EP3	2-3 minutes
	AM60				
3. Monopropylene glycol rinse (subsequent to steps 1, 2 or step 2 as appropriate)					
Die casting Extrusion	AZ91	Bright	Rinse	PG1	3-5 secs (one brief dip)
	AZ31	Metallic			

Die casting	AM50 AM60	Bright Metallic	Rinse	PG1	5-7 secs (with stirring)
4. Caustic wash (subsequent to above steps 1-3 or 2-3 as appropriate)					
All	All	All	Caustic wash	CW25	20-30 seconds
			Rinse	H <sub>2</sub> O	
5. Passivation (subsequent to above steps 1-4 or 2-4 as appropriate)					
Die casting	AZ91	Bright	Passivate	PC1	7-10 secs
		Metallic	Passivate	PC1	30-60 secs
	AM50	Bright	Passivate	PM1	7-10 secs
	AM60	Metallic	Passivate	PC1	30-60 secs
All	All	All	Electropassivate	NH <sub>4</sub> HF <sub>2</sub>	30 secs, 10-20 volts
Extrusion	AZ31	All	Passivate	PC1	30-60 secs
6 Final steps (subsequent to 1-5 or 2-5 as appropriate)					
All	All	All	Rinse	H <sub>2</sub> O	
			Dry	Hot air	

In the tables, references to concentrations and temperatures are illustrative examples only of values which provide a preferred surface finish. The processes operate over a range, both of concentrations and temperatures. Furthermore, substitutions may be made for chemical constituents; for instance, ethylene glycol may be used in place of monopropylene glycol.

- 5    Following the pre-treatment step(s), the magnesium or magnesium alloy article surface may be polished to a bright or metallic finish (step 6), or may be chemically "blasted" by a selective etch in step 5 to give a substantially light, textured finish similar to shot blasting. The method of producing these finishes is fundamentally similar in most cases and may be summarised in Table 3.
- 10   Figure 1 should be read in conjunction with the foregoing tables for details of times, temperatures and process solutions applicable to each step. The examples also provide illustrative details of how various alloys may be treated according to the present invention.

- The initial method described below may have particular application to high aluminium content alloys (for example, alloys containing greater than about 3% by weight of aluminium). Although
- 15   the overall concept remains similar for low aluminium content alloys (for example, less than about 3% by weight), the surface finish may not be as effective as that obtained by the low aluminium content polishing and/or brightening method also described below.

#### HIGH ALUMINIUM CONTENT MAGNESIUM ALLOYS

- A process of chemical or electro-chemical selective etching 3 accomplishes the removal, from
- 20   the surface being treated, of discontinuities and severe alloy component segregation. This process may also impart a somewhat controllable-altering to the texture of the surface. The term "etched" may be interchangeable replaced by "chemically blasted" (CB). The word "etched" may be reserved to describe processes as used in the pre-treatment (steps 1 to 4 in Figure 1) phases only.

- 25   An electro-chemical process using a modified phosphoric acid electrolyte may be able to "micro-polish" the surface to a high degree of brightness.

- The "electropolish" step 6 illustrated in Figure 1 and further described in Table 3 may involve two separate treatments that may be conducted in one process vessel. The first of these may be a "galvanic polish" in which the article is short-circuited to a copper counter-electrode
- 30   immersed in the EP3 / EP4 (composition given in Table 1) solution. During the galvanic polish

there is no externally imposed current.

A second, and optional treatment may be conducted during the electro-polishing and may comprise the imposition of an AC voltage, at about 5 VAC. The current may not be controlled and may therefore reach a value that depends on the surface area of the work being  
5 processed and the characteristics of the surface and alloy. A current density of 750 to 1,500 A/m<sup>2</sup> may be expected. A copper counter-electrode may be used in the electro-chemical cell/bath.

A non-damaging method for the removal of electrolyte(s) from the surface after the electro-chemical polishing step 6 may be made possible by washing the surface with a suitable  
10 electrolyte removal component in step 7. For example, following the electro-chemical polishing step 6 in which the EP3 electrolyte is used; a suitable wash (intermediary wash) may be a monopropylene glycol or ethylene glycol.

Step 7 may then be followed by an alkaline wash step 8 to neutralise any acids and further remove any electrolyte from the surface. Step 8 may then be followed by rinsing the surface  
15 with de-ionised water in step 8A prior to the surface being treated in the passivation step 9.

The resulting treated surface may then be passivated in step 9 by the anodic deposition of a transparent corrosion resistant film upon the surface, in which the deposition thickness may be controllable. A suitable corrosion resistant film may, for example, be a phosphate salt film, and such a salt may be a preferred film as a result of its useful corrosion resistance properties  
20 such as water insolubility and being slightly alkaline. The thickness of this deposited film may be varied to provide increased corrosion resistance, as well as altering the final surface finish to provide a variety of surface finishes, for example, a bright shiny surface (a thin layer of film), a metallic slightly dulled surface finish (a thicker layer of film than the bright shiny finish), and a "pearl-type" surface finish (a thicker layer of film than the metallic finish). The thickness of the  
25 film is of the order of about 100nm, although it should be noted that the thickness of the film should preferably not be around one quarter of the wavelength of visible light as interference effects will occur.

Passivation of the brightened, metallic or chemically blasted surface may be undertaken chemically, using either of PM1 or PC1 described in Table 1 or by means of an  
30 electropassivation step. As shown in Figure 2, in an electro-passivation step a DC voltage source of approximately 10-20 volts may be applied to the article to be passivated, which is made the anode of a circuit in a solution 14 of about 2% ammonium bifluoride (NH<sub>4</sub>HF<sub>2</sub>·2H<sub>2</sub>O) at ambient temperature, for about 30 seconds (refer to Figure 2 for the setup). An Aluminium



alloy counter-electrode 15 having at least twice the surface area of the article 13 being passivated may be employed. Articles to be passivated are connected to a conductive busbar which is made the anode of an electrochemical cell. Such electro-passivation methods may preferably avoid the use of heavy metals and provides substantially useful corrosion resistance.

De-ionised rinse step 10 may follow the passivation step 9 in order to remove any passivation composition components, and may then be followed by a drying step 11, which may be an air drying process. It may be desirable that a hot air dry process is employed.

Finally, this passivated surface may be treated with an inorganic, transparent and substantially corrosion resistant film, such as a solution formed by combining disodium metasilicate, a polyacrylamide coagulant and de-ionised water (IS1 - see below).

### Theory of Chemical Processing Operations

Different alloys have different chemical and surface properties depending on the alloy composition and its method of fabrication. Generally for castings, there can be large areas of phase segregation and sometimes several phases are present on the surface after cleaning. All cleaning, etching, polishing and post-treatment processes react with these different phases at different rates and produce different surface textures that may have different residual rates of reaction in corrosive environments. In the case of rolled sheet, extrusion and forged material, the metal grain size is smaller and the degree of segregation much lower, hence any treatment will produce a more uniform result.

The other major factors influencing the success of surface treatments are largely mechanical in nature. These include a variety of casting faults, dross inclusions and surface mechanical damage. Various techniques have been developed to largely overcome the problems outlined above.

### Chemical Blasting (CB) – Step 5

This is a process where iron in the process solution is reduced by the magnesium alloy and is selectively deposited on the surface as Fe or other insoluble Fe compounds. Depending on the alloy and the treatment conditions, these deposits can be controlled to give different deposition sizes and patterns. When these deposits are subsequently removed from the surface a series of pits and ridges remain on the metal surface. A surface that has a more regular geometric pattern has now replaced the original metal surface (with random defects). Hence the appearance is enhanced.

### Polishing - Step 6

This is a process that removes previously accumulated surface layers and selectively removes microscopic high points from the surface. The metal surface becomes microscopically smoother and hence more reflective or brighter.

- 5 There are two distinct processes included under this general heading;

Chemical Polishing – in which the component to be polished is suspended in the polishing solution for a certain time under fixed conditions, and Galvanic Polishing – similar to the above except that the component is electrically connected to a sheet-copper counter electrode that lines the polishing tank and a galvanic current flows between the two to give a different  
10 polishing effect.

Sometimes the galvanic method is supplemented by the imposition of an AC current at certain stages. This is done to assist in breaking diffusion stagnation and to remove surface contamination.

### Alkaline Washes – Step 8

- 15 These hot strong alkaline solutions are employed in the process schemes as a convenient method for the following:

In conjunction with surfactants, to remove oil, grease and die-lube (that is, basic cleaning).

1. To selectively remove Al, Mn and Zn from alloy surfaces.
2. To neutralise acidic films especially from the polishing process.
- 20 3. To act as a pre-conditioner and activator prior to the polishing processes.

It is recommended that two separate baths are used, one for item 1 (DGA) and the other (free of surfactant) CW25 (see Table 1) or CW10 (described below) for other purposes.

### MPG Wash – Step 7

- 25 This is basically a bath of pure mono-propylene glycol or ethylene glycol run either cold or moderately hot to act as an intermediary wash between strong phosphoric acid solutions and the alkaline wash solution. This is used so that the neutralisation reaction is less violent and may prevent the rapid stain-producing attack of dilute phosphoric acid on magnesium alloys. Accumulated water and acid in this solution can be controlled by external treatment.

### Passivation – Step 9

There are several methods of passivation of the finished surface available but the methods proposed by the present invention do not use chromium, are almost transparent, are easily controlled, can produce modified finishes and are effective against corrosion and handling damage. When used in conjunction with acrylic clear powder coatings they prevent interface corrosion and resin degradation (yellowing). They also provide a compatible, stable inter-facial layer when used in conjunction with inorganic sealing.

### **Inorganic Seal**

An inorganic sealing step is used to deposit a clear Silicon (Si) based coating over anodised or passive bright magnesium or alloy components. The coating is applied by dipping or by spraying and by adjustment of the conditions different film thicknesses can be obtained. The inorganic seal is advantageously substantially transparent and gives the substrate good protection against corrosion and mechanical damage. It can be used effectively over only a limited number of dye coloured anodised magnesium substrates as there can be a colour shift due to the high pH of the inorganic seal or in some cases the dye can be destroyed.

### **Colouring**

A limited number of colours can be applied to bright surfaces so that the metallic lustre is preserved. This is done by establishing a very thin ( $< \approx 100\text{nm}$ ), transparent film of Magnesium Oxide (MgO) on the bright substrate by a variety of means. It can then be dyed by a modified procedure using standard Aluminium (Al) dyes.

### **Chemical Processing Operations**

For the purpose of this discussion, non-anodised finishes are defined as decorative finishes that are non-opaque and largely reveal the substrate metal. The appearance can be further sub-classified as bright, metallic, pearl, etc and the texture of the substrate may be classified as flat, brushed, etched etc. As well as having the normal "silver" colour of the alloy, it is possible to produce finishes that incorporate other colours and, in general, the appearance is a "metallic" finish.

A number of procedures have been developed to produce a range of finishes and a specific procedure is chosen according to given parameters such as;

1. Appearance e.g. bright.
2. Surface texture e.g. etched.
3. Colour e.g. silver

4. Alloy e.g. AZ31, AM50.
5. Alloy form e.g. cast, rolled sheet, forged.

The following set out various examples and steps involved in treating magnesium and its alloys to achieve a brightened surface finish. They are not definitive, and are examples only to

5 illustrate preferred methodologies.

#### Example 1

A die cast plate, 140mm × 100mm, 3mm thick, of AM50 alloy, was brightened, using the following steps:

1. Degrease in CW25 at 70 °C for one minute
- 10 2. Rinse in water for approximately 30 seconds
3. Pre-etch in PE3 for 30 seconds
4. Rinse in water
5. Electropolish in EP3 solution in two stages – galvanic polish (no imposed AC voltage) for six minutes, followed by an imposed AC voltage of 5 VAC for 20  
15 seconds.
6. Rinse in monopropylene glycol for 5 seconds
7. Wash in CW25 for 20 seconds at 70 °C
8. Rinse in water
9. Passivate, using potassium permanganate solution, PM1, for 10 seconds
- 20 10. Rinse in water
11. Dry using hot air

The result was a very bright finish, having a slight yellow tinge. The die cast structure was plainly visible.

#### Example 2

25 A die cast plate of AZ91D alloy having the same dimensions as in example 1 above, was treated using the following processes:

1. Degrease in CW25, 70 °C, for 1 minute
2. Rinse in water
3. Pre-etch in PE3 for 30 seconds
- 30 4. Rinse in water
5. Polish in EP3 solution for 5 minutes, using a galvanic polish (no AC voltage)
6. Rinse in monopropylene glycol for 5 seconds
7. Wash in CW25, 70 °C for 20 seconds

8. Rinse in water
9. Passivate using PC1 for 30 seconds
10. Rinse in water
11. Dry using hot air

5 The result was a metallic finish in which casting structures were visible.

### Example 3

A die cast plate of AM50 alloy, having the same dimensions as that in examples 1 and 2 above, was treated using the following processes:

1. Degrease in CW25 at 70 °C for 1 minute
- 10 2. Rinse in water
3. Pre-etch in PE3 for 30 seconds
4. Wash in CW25, 70 °C for 30 seconds
5. Rinse in water
6. Chemical blast in three steps – 1 minute in CB2A solution followed by 7 minutes in
- 15 CB1 solution and finally, an additional minute in CB2A solution
7. Wash in CW25, 70 °C, 1 minute
8. Polish in EP3 solution in three steps – one minute using an imposed AC voltage of 5 VAC, 3 minutes without AC voltage, then an additional 20 seconds using an imposed AC voltage as before.
- 20 9. Rinse in monopropylene glycol for 5 seconds
10. Wash in CW25, 70 °C for 20 seconds
11. Rinse in water
12. Passivate in PM1 for ten seconds
13. Rinse in water
- 25 14. Dry using hot air.

The result was a bright finish, with a high degree of texturing which obscured most of the die cast structures. Examination through a microscope revealed a surface topography of sharp ridges adjacent to rounded pits.

### Example 4

30 A rolled flat plate, of AZ31B alloy, 110mm × 80mm, 1mm thick was pre-conditioned so that it was clean of sundry corrosion and dirt. It was then processed as follows:

1. Degrease in CW25, 70 °C for one minute
2. Rinse in water
3. Pre-etch in PE3 for 15 seconds

4. Rinse in water
5. Polish using four steps – 30 seconds without AC, followed by 10 seconds using an imposed AC voltage of 5 VAC, another 20 seconds without AC and finally, a further 10 seconds with the AC voltage as before
- 5 6. Rinse in monopropylene glycol for 5 seconds
7. Wash in CW25, 70 °C for 30 seconds
8. Rinse in water
9. Passivate in PC1 for 30 seconds
10. Rinse in water
- 10 11. Dry using hot air

The result was a mirror bright finish.

#### Example 5

A flat plate, AM50 alloy, of the same dimensions as those in example 1 above, was processed using the following treatments:

- 15 1. Degrease in CW25, 70 °C for one minute
2. Rinse in water
3. Pre-etch in PE3 for 15 seconds
4. Rinse in water
5. Polish in EP3 solution in two stages – galvanic polish (no imposed AC voltage) for
- 20 six minutes, followed by an imposed AC voltage of 5 VAC for 20 seconds.
6. Rinse in monopropylene glycol for 5 seconds
7. Wash in CW25 for 20 seconds at 70 °C
8. Rinse in water

The plate was then passivated by an electro-chemical treatment. It was immersed in a solution of 2% ammonium bifluoride ( $\text{NH}_4\text{HF}_2 \cdot 2\text{H}_2\text{O}$ ) which was contained in a plastic tank with attached stainless steel plates on each side. These were connected to the negative terminal of a suitable power supply while the article itself was attached to a bus-bar that was connected to the positive terminal. After twenty seconds, the power was switched on and maintained at around 15 VDC ( $\pm$  about 1 VDC). Upon the application of the electric current the article became noticeably brighter. There was no gas evolution. Initially the current was 20 Amps, but this decayed to around 1 Amp after about 5 seconds and finally to about 0.3 Amps after about 30 seconds. At this time the power was switched off, the plate was removed from the solution, rinsed with deionised water and dried. The article was bright and shiny in appearance with no obvious surface film. However, its passivity was obvious when tested using reagents towards which magnesium metal articles are normally highly reactive.

**LOW ALUMINIUM CONTENT MAGNESIUM ALLOYS (VARIANT PROCESS)**

In addition to the above mentioned examples and process steps, as an alternative, the process may be modified to provide an optimised or superior treatment for low aluminium content magnesium alloys, preferably magnesium alloys containing approximately 3% aluminium (by weight) or less. In particular, it has been discovered that this alternative surface treatment process works well with the fine-grained AZ31 alloy in either rolled sheet or extrusion form.

A new additional process solution (EP4 – described below) tailored to the special requirements of fine-grained AZ31 alloy in either rolled sheet or extrusion form has been developed for low electropolishing low aluminium content magnesium alloys. The process including EP4 solution is superior to the above described high Aluminium content method as it has fewer process steps, superior finish, reduced cost and preferably uses less energy intensive process conditions. When used in conjunction with previously defined post treatments, for example passivation, the finished material has a more aesthetic appearance and is more corrosion resistant than previously obtainable when surface treating low Aluminium content magnesium alloys using the above described high aluminium content method. In addition the process can be used with greater simplicity alongside the surface texturing or polishing process.

The following are specifications of preferred solutions and operating conditions utilised in the low Aluminium content magnesium alloy polishing or brightening method.

**Further Specifications of Solutions and Operating Conditions****Chemical polishing solution (EP4)**

750 mL MPG

115 mL H<sub>2</sub>O115 mL 69% HNO<sub>3</sub>20 mL 85% H<sub>3</sub>PO<sub>4</sub>

Temperature: 20-30 °C

**10% caustic soda (washing solution) CW10**

100 g NaOH

Water addition to make 1 L of the solution

Temperature: 70-80 °C, optimum 75 °C

**CB solution 1 (CB1)**

900 mL H<sub>2</sub>O  
50 mL 40% FeCl<sub>3</sub>  
50 mL 85% H<sub>3</sub>PO<sub>4</sub>  
Temperature: 25-40 °C

5

CB1A solution

Reduced CB1 solution  
Temperature: 25-40 °C

10 CB2A solution

Activator

780 mL H<sub>2</sub>O  
66 mL 40% FeCl<sub>3</sub>  
52 mL 3.5-3.7 % HCl

15 102 mL 2% NH<sub>4</sub>HF<sub>2</sub>16.7 g NH<sub>4</sub>Br

Temperature: 20-30 °C

Mild chemical blasting solution CB3

20 55 mL 85% H<sub>3</sub>PO<sub>4</sub>  
25 g Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O  
11 mL 40% FeCl<sub>3</sub>  
Water addition to make 1 L of the solution  
Temperature: ambient (20-25 °C)

25

Iron-(Fe) removal solution FRS2

95 mL 85% HNO<sub>3</sub>  
35 g Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.5H<sub>2</sub>O  
Water addition to make 1 L of the solution

30 Temperature: ambient (20-25 °C)

Electropassivator BPT1

30 g Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>  
51.7 g Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.5H<sub>2</sub>O

35 7.5 NaF

Temperature: 15-30 °C

Finishes: Bright – up to 70 V (except AZ31 extrusion: up to 50 V)



(Compositions shown are for 1litre of solution.)

Phosphoric etch (PE3)

605 mL 85%  $\text{H}_3\text{PO}_4$

5 365 mL  $\text{H}_2\text{O}$

30 mL 69%  $\text{HNO}_3$

Temperature: Ambient

Electropolishing solution (EP3)

10 645 mL 85%  $\text{H}_3\text{PO}_4$

323 ml monopropylene glycol:  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}$  (MPG)

32 mL  $\text{H}_2\text{O}$

Operating temperature: 35-45 °C

Important: Overheating above 50 °C is prohibited

15

Chemical polishing solution (EP4)

750 mL MPG

115 mL  $\text{H}_2\text{O}$

115 mL 69%  $\text{HNO}_3$

20 20 mL 85%  $\text{H}_3\text{PO}_4$

Temperature: 35-45 °C, optimum 40 °C

7% Caustic soda (washing solution) (CW7)

70 g NaOH

25 Water addition to make 1 L of the solution

Temperature: 70-80 °C, optimum 75 °C

Mild chemical blasting solution CB3

55 mL 85%  $\text{H}_3\text{PO}_4$

30 25 g  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

11 mL 40%  $\text{FeCl}_3$

Water addition to make 1 L of the solution

Temperature: ambient (20-25 °C)

35 Iron (Fe) removal solution FR1

15 mL 98%  $\text{H}_2\text{SO}_4$

30 mL 85%  $\text{H}_3\text{PO}_4$

Water addition to make 1 L of the solution

Temperature: ambient (20-25 °C)

Technical grade MPG (washing solution) (PG1)

- 5 Operating temperature: 35-45 °C

25% caustic soda (washing solution) (CW25)

250 g NaOH

750 mL H<sub>2</sub>O

- 10 Operating temperature: 70-80 °C

Electropassivator BPT1

30 g Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>

51.7 g Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·5H<sub>2</sub>O

- 15 7.5 NaF

Temperature: 15-30 °C

Finishes:

Bright – up to 70 V (except AZ31 extrusion: up to 50 V)

- 20 CB solution 1 (CB1)

900 mL H<sub>2</sub>O

50 mL 40% FeCl<sub>3</sub>

50 mL 85% H<sub>3</sub>PO<sub>4</sub>

Temperature: 30-40 °C

25

CB1a solution

Reduced CB1 solution

Temperature: 30-40 °C

- 30 CB2a solution

Activator

780 mL H<sub>2</sub>O

66 mL 40% FeCl<sub>3</sub>

52 mL 3.5-3.7 % HCl

- 35 102 mL 2% NH<sub>4</sub>HF<sub>2</sub>

16.7 g NH<sub>4</sub>Br

Temperature: 20-30 °C

Inorganic seal (IS1)12% Na<sub>2</sub>SiO<sub>3</sub> viscosity stabilised

Temperature: 55-65 °C

## 5 Preparation of 1 L of the seal:

- a) Dissolve 1g of "Irrigaid" polyacrylamide coagulant in 700 mL of stirred DI water until fully dissolved
- b) Slowly add 300 mL 40% Na<sub>2</sub>SiO<sub>3</sub>
- c) Filter.

10

Chemical polishing solution (EP4)

750 mL MPG

115 mL H<sub>2</sub>O115 mL 69% HNO<sub>3</sub>15 20 mL 85% H<sub>3</sub>PO<sub>4</sub>

Temperature: 30-35 °C

10% caustic soda (washing solution) CW10

100 g NaOH

20 Water addition to make 1 L of the solution

Temperature: 70-80 °C, optimum 75 °C

Mild chemical blasting solution CB355 mL 85% H<sub>3</sub>PO<sub>4</sub>25 25 g Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O11 mL 40% FeCl<sub>3</sub>

Water addition to make 1 L of the solution

Temperature: ambient (20-25 °C)

30 Iron (Fe) removal solution FRS115 mL 98% H<sub>2</sub>SO<sub>4</sub>30 mL 85% H<sub>3</sub>PO<sub>4</sub>

Water addition to make 1 L of the solution

Temperature: ambient (20-25 °C)

35

Iron (Fe) removal solution FRS295 mL 85% HNO<sub>3</sub>

35 g  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$

Water addition to make 1 L of the solution

Temperature: ambient (20-25 °C)

5 If the AZ31 (or similar low aluminium content alloy) surface is not covered in contaminants, no initial treatment to remove these is required. However, if the surface is covered with a protective corrosion resistant coating, then the FRS2 solution (which may for example be an iron removal solution) may be used to prepare the surface for subsequent treatment.

10 Further, for this alternative process the use of mixed acids in the polishing step may be used; compared to generally phosphoric acid only in the previously mentioned process for magnesium alloys having an Aluminium content of approximately 3% (by weight) or greater; together with a carrier solvent, such as monopropylene glycol (MPG). This alternative polishing step may produce an enhanced surface polish in a more controlled manner compared to the previously described process.

15 Phosphoric acid and predominantly nitric acid may comprise the preferred mixed acids utilised for the polishing step with low aluminium content surfaces. In fact, it is believed that the phosphoric acid is consequently now used as a catalytic component, rather than as a major consumable component, such as the nitric acid component. The polishing step using the EP4 solution may also be operated at approximately room temperature (~20°C); although it is appreciated that variation in the operating temperature may increase or decrease the rate of  
20 the surface treatment steps. Advantageously the components of the polishing step are consumed at lower rates, which may result in reduced frequency of polishing solution replenishment.

25 The requirement of an AC supply in the AC electro-chemical polishing step 6 becomes optional as the combined mixed acid and MPG provide sufficient polishing of the surface. The intermediary wash step 7, for example using MPG as previously described in the process above is also no longer required, and advantageously it may be that any "washing marks" resulting from the previously described intermediary process are also eliminated.

30 A variety of process steps with preferred process solutions and operating conditions may now be provided by way of example. Steps 1 to 4 may be omitted although in some cases an etching pre-treatment step may be required to remove any external protective coating from the surface.

**Surface Texturing****Heavy chemical blasting**

- |   |    |                |                                     |
|---|----|----------------|-------------------------------------|
|   | 1. | CB2A activator | 20-25 s                             |
|   | 2. | CB1A solution  | 3-6 min                             |
| 5 | 3. | FRS2 solution  | 2-2.5 min (with intensive stirring) |
|   | 4. | Water wash     |                                     |

**Mild chemical blasting**

- |    |    |                |                                     |
|----|----|----------------|-------------------------------------|
|    | 1. | CB2A activator | 20-25 s                             |
|    | 2. | CB3 solution   | 3-6 min                             |
| 10 | 3. | FRS2 solution  | 2-2.5 min (with intensive stirring) |
|    | 4. | Water wash     |                                     |

**Surface Polishing Treatments**

- |    |    |                                    |         |
|----|----|------------------------------------|---------|
|    | 1. | Chemical polishing in EP4 solution | 20-90 s |
|    | 2. | Washing in CW10                    | 15-45 s |
| 15 | 3. | Water wash                         |         |

**Post-treatment**

1. Passivation (BPT1, voltage according to desired finish)
2. Water wash
3. Dry

**20 An Experimental set-up**

A brightening process was trialled and was conducted in a 2000ml beaker at 20 to 30 °C in EP4 solution.

The bath was stirred with a mechanical stirrer and its temperature recorded.

- At various intervals the bath conductivity was measured and small samples of EP4 were removed for later analysis. Weight loss measurements were made on the Magnesium test plates at regular intervals as well as the amount of EP4 drag-out. All measured parameters have been evaluated as a function of the cumulative area processed.

Typical sample plate processing consisted of;

- 10 1. Test plates were AZ31 alloy (Spectrolite) sheets 110 x 80 x 1.2 mm. Total area 0.0176 m<sup>2</sup> each. Plates were recycled for a number of process runs and hence only one pre-treatment in dilute nitric acid was given for each new plate introduced.
2. Plate accurately weighed.

3. Plate polished in EP4 for 2 min and drained for 10 sec.
4. Plate washed in 10% NaOH for 15 sec.
5. Plate rinsed in DI water for 10 to 15 sec, hot air dried and reweighed.

5 The brightness of the finished plates were monitored and some plates were passivated in BPT2 solution to obtain either bright, metallic or pearl finishes to assess this process.

Any passivated plates were stripped in dilute nitric acid after assessment before return to the start of the process.

#### Results:

- 10 1. A total of 247 test plates were processed through the polishing bath with no chemical replenishment during this time. The total area processed was 4.488m<sup>2</sup> or 2.244 m<sup>2</sup>/L.
2. The cut-off point for the trial was defined to be when the metal removal rate (MMR) fell to less than 60% of the initial rate.
3. All test plates were brightened very satisfactorily up to the end of the trial.
- 15 4. After the trial had ended a replenishment was made to the bath and the results measured were in close agreement with prediction.
5. The experimental data fits the bath operating model. This model accounts for both component consumption and dragout.
- 20 6. Satisfactory methods have been developed for the analysis of Magnesium, total acid, MPG, phosphate, nitrate and MRR.

This process has proven to be capable of producing excellent results on fine-grained AZ31 sheet in a very consistent manner.

The process is simple, has few steps and utilises relatively low cost chemicals and simple low cost plant and equipment. The process is easily managed using simple laboratory tests.

- 25 The bath is easily maintained with a two-part addition mixture on a periodic basis.

#### General Procedure (and codes) for All Finishes

- |                         |   |
|-------------------------|---|
| 1. Pre-treatment(s)     | E |
| 2. Surface texturing    | X |
| 30 3. Surface treatment | S |
| 4. Post-treatment(s)    | T |
| 5. Colouring (optional) | C |

**Examples of Procedures****Pre-treatments**

E0- No pre-treatment step

E1

Step No.	Operation	Chemicals	Temp. °C	Time min
1	Degrease*	DGA	70-80	5
2	Water rinse*	Tap	15-50	0.5-1
3	Phosphoric etch	PE3	15-35	0.5
4	Water rinse	Tap	15-50	0.5-1
5	Alkaline wash	DGA	70-80	1-1.5
6	Water rinse	Tap	15-50	0.5-1

5 \* These steps can be omitted if metal surface does not have lubricants

E2

Step No.	Operation	Chemicals	Temp. °C	Time min
1	Degrease	CW25	70-80	2-3
2	Water rinse	Tap	15-50	0.5-1

**Illustrative Surface Texturing (CB)**

X0-No Surface texturing step

10 X1

Step No.	Operation	Chemicals	Temp. °C	Time min
1	Activation	CB2a	30-40	0.3
2	Chemical blast	CB1 (CB1a)	30-40	1-5
3	Alkaline wash	CW25	70-80	5
4	Water rinse	Tap	15-50	0.5-1

X2

Step No.	Operation	Chemicals	Temp. °C	Time min
1	Chemical Blast	CB1 (CB1a)	30-40	1-6
2	Alkaline wash	CW25	70-80	5
3	Water rinse	Tap	15-50	0.5-1

X3

Step No.	Operation	Chemicals	Temp. °C	Time min
1	Activation	CB2a	30-40	0.3-0.5
2	Chemical blast	CB3	30-40	1-5
3	Iron removal	FR1	20-40	0.5-1.5

4	Water rinse	Tap	15-50	0.5-1
---	-------------	-----	-------	-------

**Illustrative Surface Treatments****S1**

Step No.	Operation	Chemicals	Temp. °C	Time min
1	Chemical polish	EP3	35-45	2
2	Galvanic polish	EP3	35-45	2-3
3	Chemical polish	EP3	35-45	1-1.5
4	Glycol wash	PG1	35-40	0.3
5	Alkaline wash	CW25	70-80	1.5-2
6	Water wash	Tap	20-40	0.5-1

**5 S2**

Step No.	Operation	Chemicals	Temp. °C	Time min
1	AC polish	EP3	35-45	1
2	Galvanic polish	EP3	35-45	3-4
3	AC polish	EP3	35-45	0.3-0.5
4	Glycol wash	PG1	35-40	0.3
5	Alkaline wash	CW25	70-80	0.5-1
6	Water wash	Tap	20-40	0.5-1

**S3**

Step No.	Operation	Chemicals	Temp. °C	Time min
1	Chemical polish	EP3	35-45	2
2	Galvanic polish	EP3	35-45	1-1.5
3	AC polish	EP3	35-45	0.2-0.5
4	Glycol wash	PG1	35-40	0.25-0.3
5	Alkaline wash	CW25	70-80	0.5-1
6	Water wash	Tap	20-40	0.5-1

**S4**

Step No.	Operation	Chemicals	Temp. °C	Time min
1	Chemical polish	EP4	35-45	0.3-2
2	Alkaline wash	CW7	70-80	0.2-0.75
3	Water wash	Tap	20-40	0.5-1



**Illustrative Post-treatments (Passivation)****T1 (Bright)**

Step No.	Operation	Chemicals	Temp. °C	Voltage V	Time min
1	Electro-passivation	BPT1	15-30	40-70	2
2	Water rinse	DI water	15-30	-	0.5-1
3	Hot air dry	-	70-110	-	1

**T2 (Metallic)**

Step No.	Operation	Chemicals	Temp. °C	Voltage V	Time min
1	Electro-passivation	BPT1	15-30	90-100	2
2	Water rinse	DI water	15-30	-	0.5-1
3	Hot air dry	-	70-110	-	1

5

**T3 (Pearl)**

Step No.	Operation	Chemicals	Temp. °C	Voltage V	Time min
1	Electro-passivation	BPT1	15-30	115-125	2
2	Water rinse	DI water	15-30	-	0.5-1
3	Hot air dry	-	70-110	-	1

**Treatment Component Table**

Procedure codes are shown in table below.

Finish/Alloy	AZ31 extrusion or sheet*	AM50 cast	AZ91cast
Flat			
Bright	E0+S4+T1	E1+S2+T1	E1+S1+T1
Metallic	E0+S4+T2	E1+S2+T2	E1+S1+T2
Pearl	E0+S4+T3	E1+S2+T3	E1+S1+T3
CB			
Bright	E0+X3+S4+T1	E1+X1+S2+T1	E1+X1+S1+T1
Metallic	E0+X3+S4+T2	E1+X1+S2+T2	E1+X1+S1+T2
Pearl	E0+X3+S4+T3	E1+X1+S2+T3	E1+X1+S1+T3

10

**Results from Salt Spray (Corrosion testing) of Treated Surfaces:**

Salt spray testing was conducted on samples of AZ31 alloy sheet or extrusion which had been brightened or polished according to the above described low Aluminium content method to determine resistance to corrosion.

#### 5 Sample preparation:

The samples were prepared using following technique:

1. No pre-treatment for clean metal (sheet or extrusion)
2. Surface cleaning by FRS2 solution (Spectrolite sheet)
3. CB2A\* 20 s
- 10 4. CB1A (heavy blasting) or CB3 (mild blasting)\* 3 min
5. FRS2\* 2 min
6. EP4 1 min
7. CW10 15-30 s
8. Water wash
- 15 9. BPT1 1 min
10. Water wash
11. Drying
12. Acrylic powder coating#

20 \* For CB finishes only

# When required

#### List of samples

Sample	Alloy	No of samples	Finish	Passivating voltage, V	Commentary
CN1	AZ31, Spectrolite sheet	2	Mild CB, bright, CB2A+CB3	50	Powder coated
CN2	AZ31	2	Coarse CB, bright, CB2A+CB1A	50	Powder coated
CN3	AZ31	2	Mild CB, bright, CB2A+CB3	50	Powder coated
CN4	AZ31	2	Mild CB, metallic, CB2A+CB3	90	Powder coated
CN5	AZ31	2	Mild CB, pearl, CB2A+CB3	120	Powder coated
CN6	AZ31	2	Flat, bright	50	Powder

					coated
CN7	AZ31, extrusion	2	Mild CB, bright, CB2A+CB3	50	Powder coated
CN8	AZ31, extrusion	2	Coarse CB, bright, CB2A+CB1A	50	Powder coated
CN9	AZ31, extrusion	2	Flat, bright	50	Powder coated
CN10	AZ31, Spectrolite sheet	2	Heavy CB, bright, CB2A+CB1A	50	Powder coated
CN11	AZ31	2	CB, bright	50	No powder coating
CN12	AZ31	2	CB, metallic	90	No powder coating
CN13	AZ31	2	CB, pearl	120	No powder coating

### Experimental results

Sample	Alloy	Finish	Passivation	Protective coating	Hours in salt spray	Commentary
Passivated metal (passivated, no protective acrylic coating)						
CN11	AZ31	CB, bright	BPT1	No coating	24	Significant pitting corrosion on front side. Rear side: no corrosion
CN12	AZ31	CB, metallic	BPT1	No coating	24	As above
CN13	AZ31	CB, pearl	BPT1	No coating	24	As above
Bright finish (passivated, acrylic coating)						
CN1	AZ31, Spectrolite sheet	Mild CB, bright, CB2A+ CB3	BPT1	Powder coating	48	Heavy corrosion on the top and on the bottom of the sample. Uncoating of acrylic layer
CN2	AZ31	Coarse CB, bright, CB2A+	BPT1	Powder coating	48	As above

		CB1A				
CN3	AZ31	Mild CB, bright, CB2A+ CB3	BPT1	Powder coating	48	As above
CN6	AZ31	Flat, bright	BPT1	Powder coating	48	Heavy corrosion
CN7	AZ31, extrusion	Mild CB, bright, CB2A+ CB3	BPT1	Powder coating	24	Pitting corrosion The sample could endure additional 24 hours. Corrosion was caused by uneven powder coating
Sample	Alloy	Finish	Passivation	Protective coating	Hours in salt spray	Commentary
CN8	AZ31, extrusion	Coarse CB, bright, CB2A+ CB1a	BPT1	Powder coating	48	Heavy filiform corrosion Sample had imperfect powder coating: brown colour on the top of CB hills
CN9	AZ31, extrusion	Flat, bright	BPT1	Powder coating	48	Heavy bottom corrosion. Uncoating of acrylic layer
CN10	AZ31, Spectrolite sheet	Heavy CB, bright, CB2A+ CB1A	BPT1	Powder coating	48	As above
Metallic finish (passivated, acrylic coating)						
CN4	AZ31	Mild CB, metallic, CB2A+ CB3	BPT1	Powder coating	168	Corroded from edges with uncoating of acrylic layer
Passivated samples + acrylic powder coating (local)						
CN5	AZ31	Mild CB, pearl, CB2A+ CB3	BPT1	Powder coating	336	Middle part of samples in good conditions. Edge corrosion only

**Corrosion Testing Conclusions**

Corrosion resistance of passivated (BPT1) and powder coated (optionally) AZ31 samples was tested. Spectrolite sheet and extrusion were used in the experiments.

5

**Tolerance to salt spray**

- |       |  |   |
|-------|--|---|
| 1.    | Sheet (bright, not passivated, powder coated)          | - less than 24 hrs<br>(from previous experiments) |
| 2.    | Sheet (passivated, not powder coated)                  | - up to 24 hours                                  |
| 10 3. | Sheet or extrusion (bright, passivated, powder coated) | - 48 hrs  |
| 4.    | Sheet (metallic, passivated, powder coated)            | - 168 hrs   |
| 5.    | Sheet (pearl, passivated, powder coated)               | - 336 hrs   |

15 Relatively low corrosion resistance of bright passivated AZ31 alloy presumably is due to uneven powder coating (extrusion) and small thickness of plates (0.8 mm sheet). The latter produced centres of corrosion on the sample edges.

Aspects of the present invention have been described by way of example only and it should be appreciated that modifications and additions may be made thereto without departing from the scope thereof as defined in the appended claims.

CLAIMS

1. A method of polishing and/or brightening a magnesium or magnesium alloy surface comprising the steps of:

- 5           i) polishing the surface, and  
          ii) passivating the polished surface.

2. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in claim 1, wherein the method further comprises an initial step of pre-treating said surface to remove surface contaminants.

10 3. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in claim 1 or claim 2, wherein said pre-treating step comprises chemically etching said surface and/or degreasing said surface.

4. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in claim 2 or claim 3, wherein surface contaminants are removed prior during the pre-treatment step by contacting said surface with one or more degreasing components, such as sodium hydroxide.

5. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in claim 3, wherein said chemical etching component is nitric acid solution and/or phosphoric acid.

20 6. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in any one of claims 1 to 5, wherein the polishing step is carried out by a chemical polish and/or electro-chemical polish while said surface is immersed in a polishing composition.

7. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in claim 3, wherein said chemical polish and/or electro-chemical polish removes surface layers and/or reduces microscopic high points from the surface.

8. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in any one of the preceding claims, wherein polishing step is carried out by immersing said surface in a bath of one or more of the following components; a phosphoric acid solution, monopropylene glycol, ethylene glycol, and nitric acid.

30 9. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in any one of the preceding claims, wherein said electro-chemical polish is a galvanic electrolysis.

10. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in any one of the preceding claims, wherein said electrochemical process further includes the supply of an external voltage to said surface.
- 5 11. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in any one of the preceding claims, wherein during said electro-chemical polish an electrolyte anti-stagnation means is utilised or an AC voltage is applied to the electrolyte containing said surface.
- 10 12. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in any one of claims 5 to 11, wherein said electrolyte anti-stagnation means is an electrolyte stirrer and/or an ultrasonic wave generating means.
13. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in claim 12, wherein said polishing step is followed by an intermediary wash removing at least some of the chemical and/or electrolyte solution from said surface.
- 15 14. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in claim 13, wherein said intermediary wash is carried out in a composition containing monopropylene glycol and/or ethylene glycol.
15. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in any one of the preceding claims, wherein said polishing step and/or said intermediary wash is followed by an alkaline wash.
- 20 16. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in claim 15, wherein said alkaline wash is carried out in a composition containing sodium hydroxide.
- 25 17. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in claim 15 or claim 16, wherein said alkaline wash substantially neutralises acids and/or substantially removes Aluminium, Manganese or Zinc from said surface.
18. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in any one of the preceding claims, wherein said passivating step provides a substantially corrosion resistant and/or water insoluble surface coating or film.
- 30 19. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in claim 18, wherein said substantially corrosion resistant and/or water insoluble surface coating or film is a phosphate salt coating or film.
20. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in claim 18 or claim 19, wherein said passivating step voltage is varied to alter said substantially corrosion resistant and/or water insoluble surface coating or film thickness.

21. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in any one of the preceding claims, wherein an inorganic material coating or sealer is applied to said substantially corrosion resistant and/or water insoluble surface coating or film.

5 22. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in claim 21, wherein said inorganic material coating or sealer is substantially transparent and/or substantially provides corrosion protection and/or at least provides some protection from mechanically induced damage.

10 23. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in claim 21 or claim 22, wherein said inorganic material coating or sealer is a silicon based composition, such as a disodium metasilicate, and a polyacrylamide coagulant in de-ionised water.

15 24. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in any one of the preceding claims, wherein said passivating step and/or said inorganic material coating or sealer step is followed by a surface drying step.

25. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in any one of the preceding claims including the pre-treatment steps of:

a. immersing the surface in an iron based solution,

20 b. activating said surface with said iron based solution, wherein said iron based solution is reduced to thereby deposit iron on said surface,

c. etching said surface with an etch composition to modify the activated surface layer,

d. stripping iron deposits from said surface with an iron removal composition, and

25 e. washing said surface to substantially remove compositions remaining on said surface.

26. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in claim 25, wherein said activator is a solution selected from the following; ferric chloride, hydrochloric acid, ammonium bifluoride, and ammonium bromide.

30 27. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in claim 25 or claim 26, wherein said etch composition is selected from the following; ferric chloride; ferric chloride and phosphoric acid solution, or a reduced solution of ferric chloride and phosphoric acid.



28. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in claim any one of claims 25 to 27, wherein said iron removal composition is selected from the following; nitric acid and sodium borate in solution, or nitric acid and phosphoric acid in solution.

5 29. A method of polishing and/or brightening a magnesium or magnesium alloy surface as claimed in any one of claims 25 to 28, wherein said step of washing said surface is carried out with a water wash or an alkaline wash.

10 30. A method of polishing and/or brightening a magnesium or magnesium alloy surface substantially as hereinbefore described and with reference to any one of the accompanying drawings.

31. A magnesium or magnesium alloy surface polished or brightened according to the method substantially as hereinbefore described and with reference to any one of the accompanying drawings.

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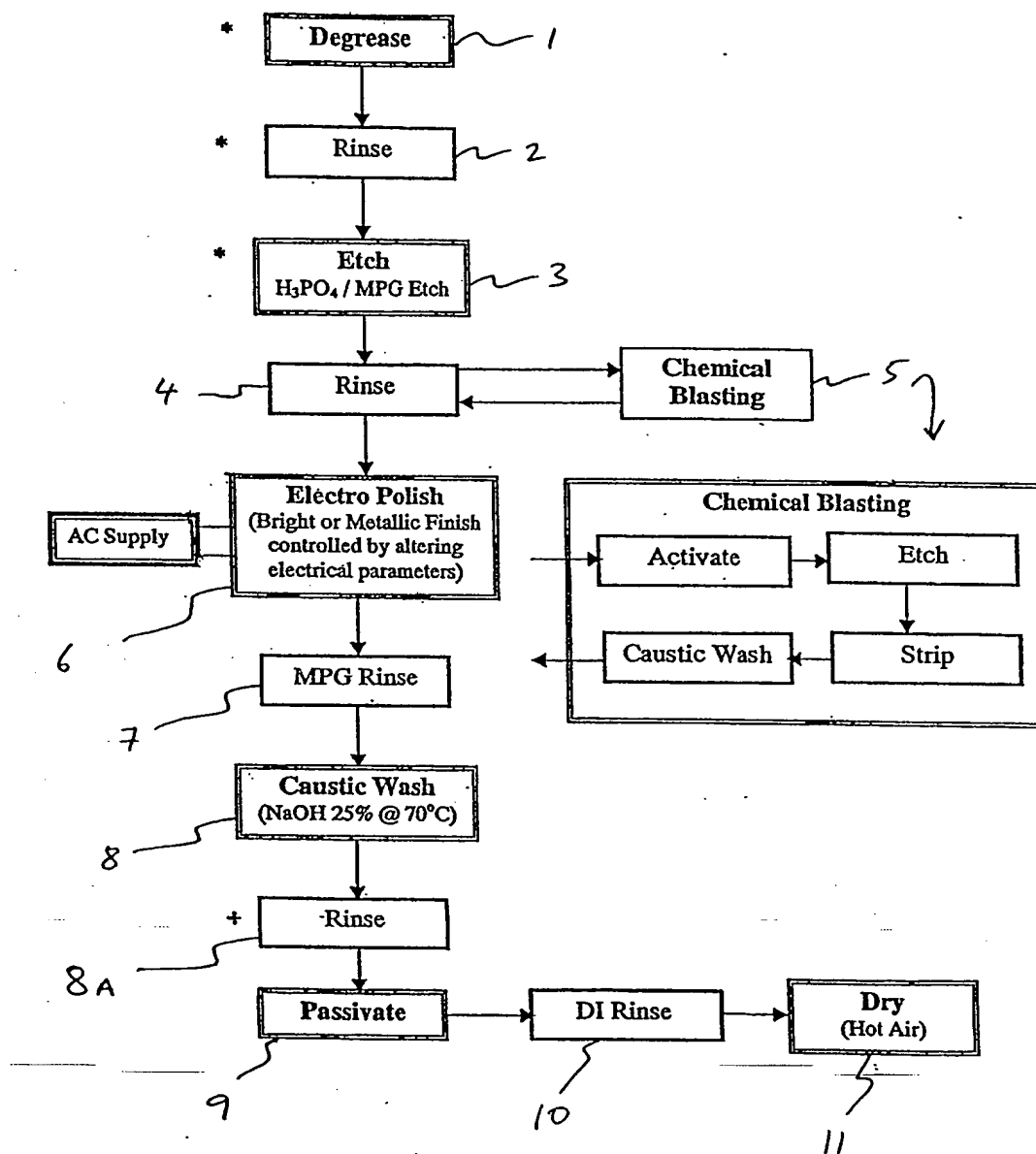


FIGURE 1

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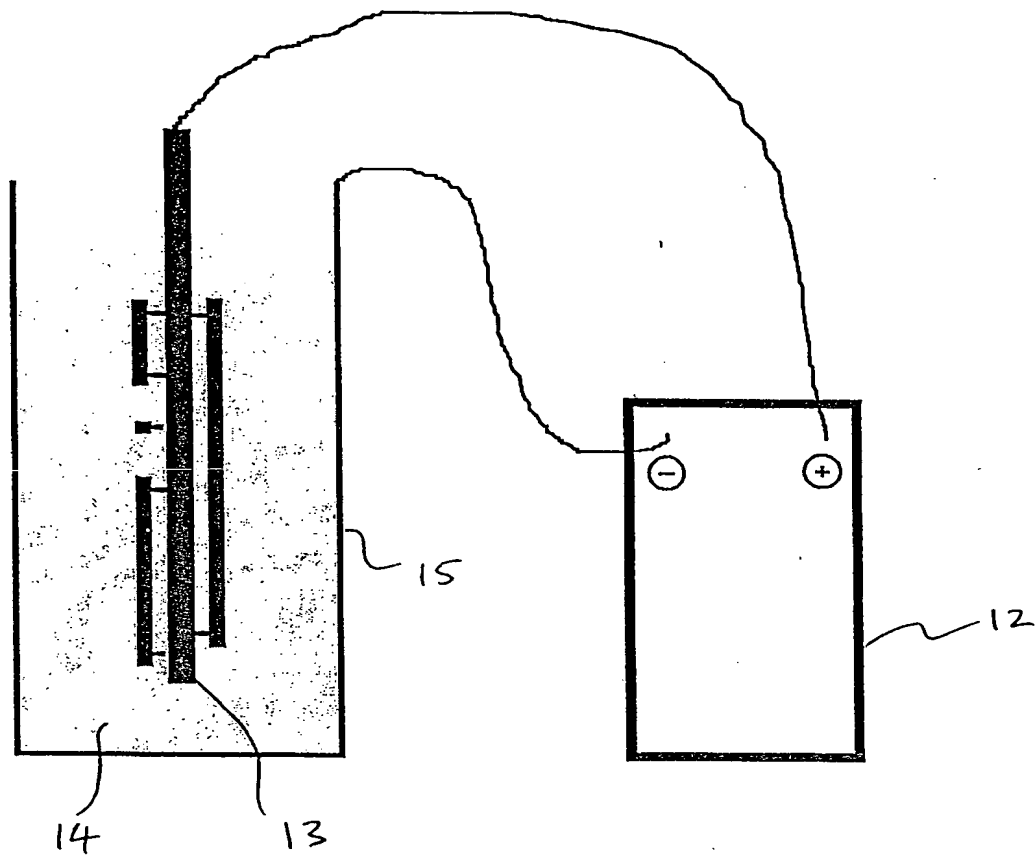


FIGURE 2

**A. CLASSIFICATION OF SUBJECT MATTER**

Int. Cl. <sup>7</sup>: C25D 11/30, 11/36, 11/38

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DWPI: C25D 11/30, 11/36, 11/38; C23F 1/22, 1/40, 3/00, 3/02, 3/04, 17/00; C25F 3/04, 3/18; C23C 22/-

Keywords: magnesium, polish+, etch+, brighten+, clean+, pickl+, passivat+, anodis+, anodiz+, phosphatis+, phosphatiz+, chromatis+, chromatiz+, phosphatiz+, conversion coat+

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstract Accession No. 93-231391/20, Class A88, E14, G03, M14 (A21, A25, A35) EP 908632 A (VOLKSWAGEN AG) 14 April 199 Abstract	1-3
X	Derwent Abstract Accession No. 1999-395987/34, Class A35, E14, M13, (A21, A25, A81, A95, E19, E34, E36) DE 19800035 A (VOLKSWAGEN AG) 8 July 1999 Abstract	1-3, 18-19
X	WO 0044557 A (HENKEL CORPORATION) 3 August 2000 Whole document	1-3, 18-19

☒ Further documents are listed in the continuation of Box C

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"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
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Date of the actual completion of the international search  
15 December 2003

Date of mailing of the international search report

1-9 DEC 2003

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/NZ03/00200

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6319819 B (BESSER ET AL) 20 November 2001 Whole document	1-31
A	US 6596150 B (NISHINO ET AL) 22 July 2003 Whole document	1-31

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/NZ03/00200

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member			
DE	19800035	NONE			
EP	0908632	DE	19744312		
WO	0044557	JP	2000219975		
US	6319819	NONE			
US	6596150	EP	0960743	JP	2000043436
		US	2002153253	JP	2000043441
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